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Micro- and Nanostructures from Liquid Crystalline Cellulose Materials

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14. ABSTRACT

The objective of the project was to produce, for the first time, helical gold cellulosic nano and micro wires. Electrospinning was used to produce right and left handed fibers. The use of these helical objects, as templates for gold nanoparticles, implicated the control of the helices pitch and diameter and also the separation of the right from left handed helices. To achieve this performance it was crucial to understand the mechanism that was responsible for the helical winding. In order to investigate the origin of the intrinsic curvature found in the cellulosic fibers, morphological and structural features were investigated by means of nuclear magnetic resonance imaging (MRI) and polarizing optical microscopy (POM). POM images and MRI measurements indicated that the presence of off-axis disclination lines, embedded in the cylindrical fibers, was the explanation for the observed helical winding. Preliminary MRI results indicate that the presence of gold nano particles enhanced the intrinsic curvature of the fibers by promoting the existence of more disclinations lines defects along the fiber.

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Micro- and Nanostructures from Liquid Crystalline Cellulose Materials

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1 March 2010 to 28 February 2011

Comprehensive summary of the significant work accomplished.

The first part of the results presented in this report was published in **Soft Matter**, 2010, 6, 5965, DOI: 10.1039/c0sm00427h and considered as “Featured Research” by **SoftMatterWorld Newsletter**, 22, 2010.

The final part of the report concerns original results that are not published and are under investigation.

Helical and spiral conformations which can be found in biological systems, such as plant tendrils, curled hair or snail shells can also be observed in fibers obtained by electrospinning of cellulosic liquid crystalline solutions (fig.1). Remarkably, however, previous studies indicate that fibers produced from right-handed cholesteric cellulosic solutions could wind with either left- or right-handed helicity, which rules out a direct relationship with the chirality of cellulose and the underlying cholesteric mesophase. From March 2010 to February 2011 the work performed, in the framework of the project, was to understand the mechanism responsible for the helical winding of the electrospun cellulosic fibers, in order to control the helicity and the handness of the fibers to be used as templates for gold nano wires.

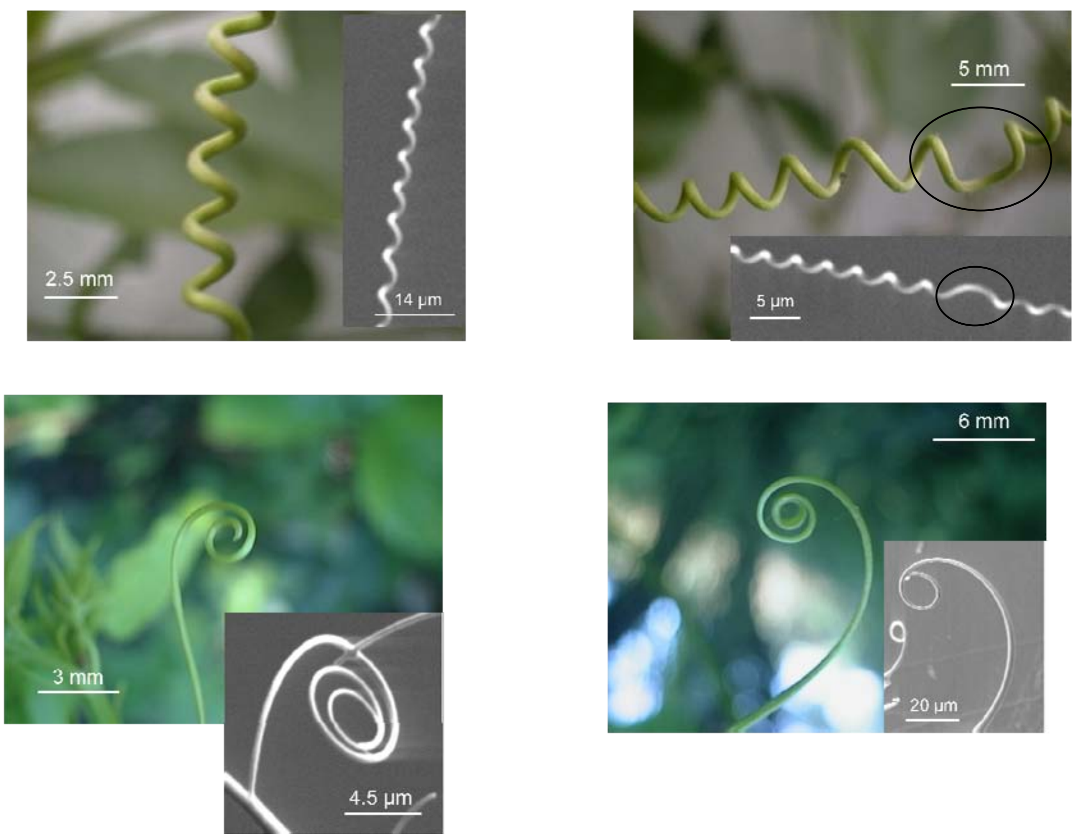

Figure 1 Helices and spirals in Passiflora edulis (optical photographs) and in electrospun cellulosic microfibers (SEM images). Helices form when the tendril or fiber is connected at both ends and torsion is released; spirals when the tendril or fiber is connected at one end only. Helix reversals “perversions” are clearly seen in both systems (marked by black circles).

Cellulosic micro and nano fibers were produced from viscous iridescent liquid crystalline solutions (60%w/w) of acetoxypropylcellulose (APC) (prepared according literature [1]) in anhydrous dimethylacetamide (DMAC). The solution was poured into a 1 ml syringe fitted with variable diameter needles (average diameter 0.15 to 0.2 mm), which was then placed in a infusion syringe pump (KDS100) to control the polymer solution feed rate. A conducting ring, 15 cm in diameter, was held coaxially with the needle tip at its centre, and electrically connected to it. The needle plus ring were directly connected to the positive output of a high voltage supply (Glassman EL 30kV). After applying the electric potential between the metallic syringe-tip and the plate, the anisotropic APC solution was continuously fed to the syringe-tip at a constant flow rate 0.04 mlh^{-1}, and accelerated by the ensuing electric field towards a collector consisting of two conductive strips separated by a void gap of 1 cm. The optimized operating conditions for the continuous drawing of the fibers were at a voltage of 15kV for a distance between the nozzle and collector equal to 20 cm (Figure 2 represents the apparatus used).

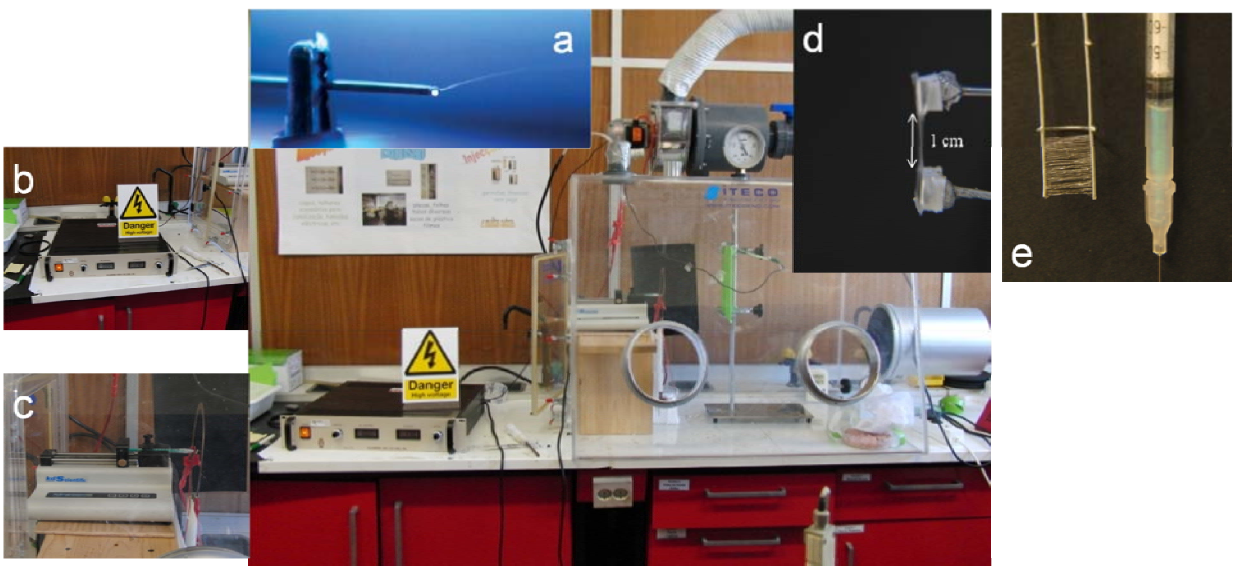

Figure 2 Background represents the electrospinning apparatus mounted in a glove chamber. a. detail showing a fiber coming out from the nozzle; b. high voltage supply (Glassman EL 30kV); c. infusion syringe pump (KDS100); d. collector consisting of two conductive strips separated by a void gap of 1 cm; e. Fibers aligned between the two electrodes and syringe with the anisotropic iridescent cellulosic solution.

In order to investigate the origin of the intrinsic curvature found in the cellulosic fibers the precursor cellulosic solutions were introduced in straight glass capillaries and forced, by continuous movement of the cellulosic solution, to produce a jet at the end of the capillary. The flow inside the capillaries and the jet at the end of them were observed. Depending on the shear rate and on the liquid crystalline characteristics of cellulosic solutions, the jet showed spontaneous curvature and torsion. Nuclear magnetic resonance imaging (MRI) analysis allowed imaging of characteristic structure at chosen filament cross section along the capillary tube. Isotropic solutions confined in the capillary, which generate straight electrospun fibers,

showed a homogenous symmetric cross-section structure, implying that the averaging of different structural features would maintain a straight fiber conformation. Confined liquid crystal phases, which generate helical fibers, showed a heterogeneous structure in cross-section with black spots predominantly located closest to the tube walls and never at the middle of the tube. The off-axis position of the black spots varied along the tube. Polarizing Optical Microscopy (POM) confirmed that the black spots corresponded to the core of a linear topological defect (disclination) which could be observed in anisotropic presheared solutions above a certain critical shear rate (Figure 3 and Figure 4).

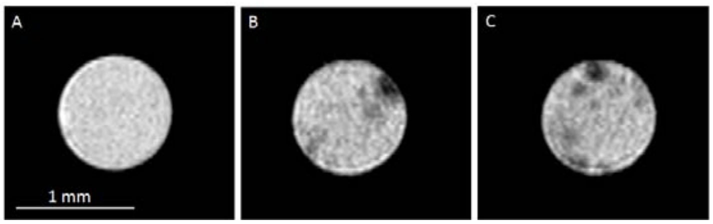

Figure 3 MRI images of the cross section of a capillary filled with (A) an isotropic solution (20% w/w, APC/DMac) and B and C a liquid crystalline solution (60% w/w, APC/DMac) in subsequent cross-sections.

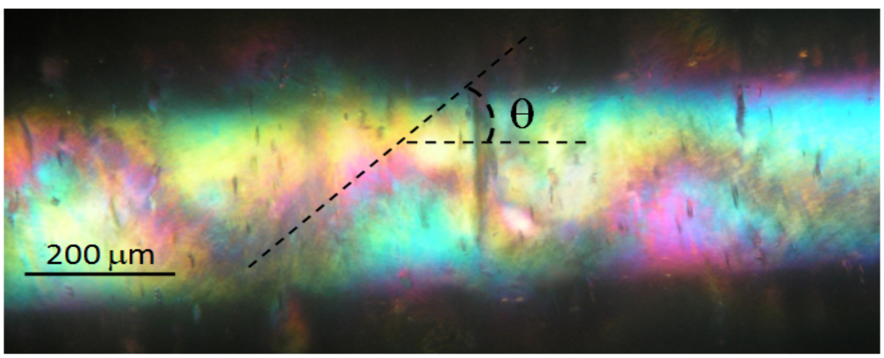

Figure 4 POM image showing that the defects lines were forming a helix along the capillary tube for anisotropic liquid crystalline solutions

The consequence of the intrinsic curvature of fibers is remarkable and may be observed during the thinning and break-up of jets produced by continuous motion of cellulosic liquid crystalline solutions (fig.5).

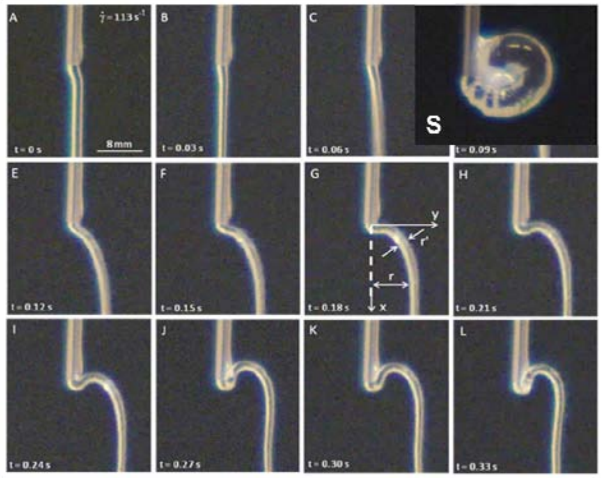

Figure 5 Shape of a cellulosic jet after gravitational drainage of the “snail” (S) material accumulated at the end of the needle. (A) through (L) show the time sequence illustrating the formation of a back-bending flow. The motion of the jet requires the subtle combination of different effects: initial shear rate (formation of an initial bent jet), free- end boundary conditions and fiber tapering due to the added tension.

Some preliminary MRI results, which will be deeply investigate during next year, indicate that the presence of gold nano particles enhanced the intrinsic curvature of the fibers by promoting the existence of more disclinations lines defects along the fiber.

Cellulosic anisotropic solutions with inorganic nanoparticles (0.47% w/w) were electrospun and two main features were observed; first, the curling of the jets at the end of the glass is achieved for much lower shear rates, second, the electrospun fibers, due to the much higher intrinsic curvature, adopt more complex entangled conformations (figure 5) which are in accordance with the MRI measurements (see figure 6).

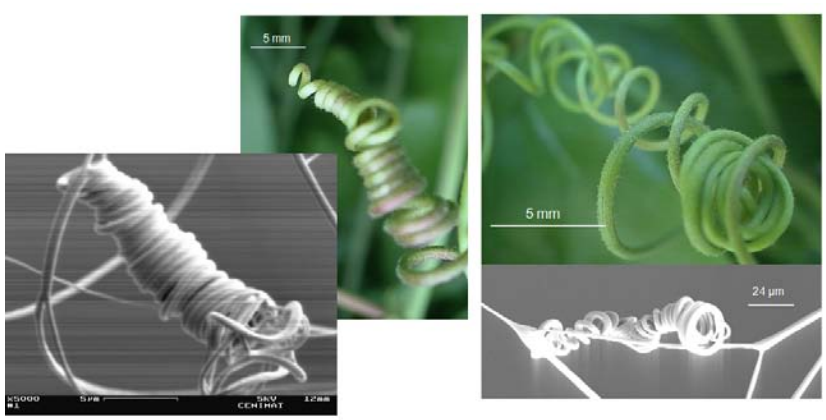

Figure 5 Passiflora edulis tendrils (optical photographs) electrospun cellulosic/nano inorganic particles microfibers (SEM images). Complex entangled conformations.

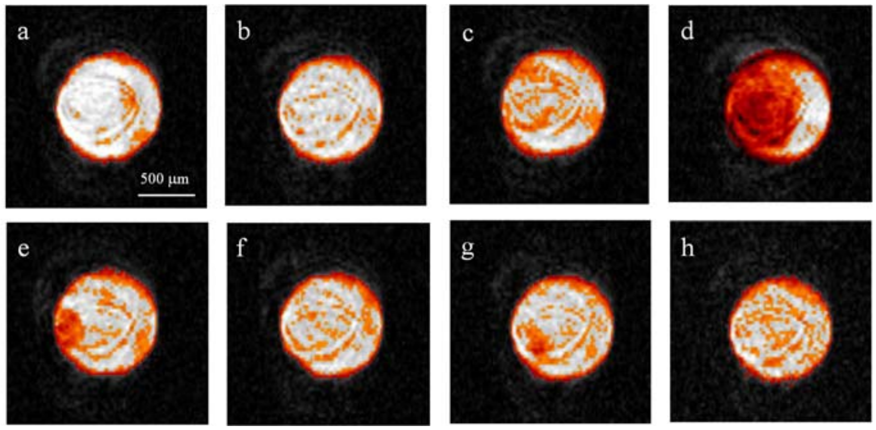

Figure 6 MRI images of the cross section of a capillary filled with a liquid crystalline solution with nano inorganic particles (60% w/w, APC/DMac and 0.47% w/w of nano particles) in subsequent cross-sections. A Higher percentage of defects can be observed (studies are underway).